

On the Equilibrium Shape of an Ice Crystal

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Abstract: We examine the shape of a an isolated, dislocation-free ice crystal when it is in equilibrium with the vapor phase in an isothermal closed environment, as a function of temperature. From our analysis we draw the following conclusions: 1) The equilibrium shape has not yet been definitively measured for ice crystals; 2) The surface energy anisotropy is likely cusp-like near the facet angles, and the size of the cusps can be estimated from crystal growth measurements; 3) The equilibrium shape is likely nearly spherical with only small faceted regions; 4) The time needed to reach equilibrium is likely prohibitively long, except under special circumstances; and 5) Surface energy effects likely play a relatively smaller role in ice crystal growth dynamics when compared to the role of attachment kinetics.

1 Introduction

Studies of the equilibrium crystal shape (ECS) for a given material are useful for understanding several static surface properties, such as surface energy anisotropies and step energies, and can also yield important insights into dynamical properties such as step-step interactions, surface diffusion, and crystal growth behavior. For this reason there has been much interest in ECS measurements and theory over the past several decades, and there is a considerable literature on the subject (for example see the review articles [1, 2, 3]).

For many simple metals that have been studied, the surface energy anisotropies are fairly small, typically a few percent difference between surfaces of maximum and minimum energy [4, 5, 6, 7]. The typical ECS is nearly spherical with small flats at the lower-surface-energy facet surfaces, corresponding to cusps in the surface energy (i.e. the surface energy $\gamma(\hat{n})$ has a discontinuous first derivative at each facet angle, where \hat{n} is the surface normal unit vector). The ECS can be derived from $\gamma(\hat{n})$ using the well-known Wulff construction, showing that the size of the cusps relates to the size of the corresponding facet surfaces in the ECS. Adsorbates may also substantially change $\gamma(\hat{n})$ and the ECS [8].

We consider here the ECS of an isolated, dislocation-free ice crystallite when it is in equilibrium with the vapor phase in an isothermal closed environment, as a function of temperature. The questions we wish to address include:

- 1) What is known about the ice ECS and surface energy anisotropies?
- 2) What experiments have been done to date, and what have they revealed?
- 3) What are the prospects for new experimental studies?
- 4) What role does surface energy play in ice growth from water vapor?

2 Lowest Order Theory

For a vicinal surface tilted a small angle θ from the facet angle, we can write the surface energy as $\gamma(\theta) \approx \gamma_{facet} + \gamma_{steps}(\theta)$, where γ_{facet} is the surface energy of a flat facet surface and $\gamma_{steps}(\theta)$ is the additional surface energy that arises from molecular steps on the surface [9]. To lowest order, neglecting step-step interactions, this becomes

$$\gamma(\theta) \approx \gamma_{facet} + \frac{\beta}{a} \sin \theta$$

where β is the step energy per unit length and $a \approx 0.32$ nm is the step height. Plugging this into the Wulff construction then yields the half-angle of the facet surface (as seen from the center of the crystallite) for the ECS [9]

$$\theta_{HW,facet} \approx \frac{\beta}{a\gamma_{facet}}.$$

For the surface energy of a basal or prism facet we estimate $\gamma_{facet} \approx 0.08$ J/m² [10, 11, 12], and measurements of crystal growth yield $\beta \approx 1 \times 10^{-12}$ J/m for temperatures between -2 and -10 C [13, 14], giving $\theta_{HW,facet} \approx 0.04$ radians. If two basal facets and six prism facets are present with similar $\theta_{HW,facet}$ values, then the total fraction of the ECS surface area that is faceted is approximately $f \approx 8\pi\theta_{HW,facet}^2/4\pi^2 \approx 0.1$ percent. This fraction increases at lower temperatures, as β is a strong function of temperature, and at -40 C we find $f \approx 2$ percent. The biggest uncertainty in this calculation is our knowledge of the step energy β , which has been derived indirectly, from 2D nucleation dynamics in crystal growth observations.

Overall the surface energy $\gamma(\hat{n})$ of the ice-vapor interface is not well known, either on the facet surfaces or on unfaceted surfaces. Determining the absolute value of $\gamma(\hat{n})$ is difficult, and experiments to date yield have yielded results with substantial uncertainties. Calculations are also quite uncertain because the detailed surface structure of ice is rather poorly understood, especially surface melting and other surface restructuring, and this strongly affects estimates of $\gamma(\hat{n})$. The anisotropy of $\gamma(\hat{n})$ could be obtained from observations of the ECS, but experiments to date are not definitive (see below). Nevertheless, in my opinion the measurements do indicate with some confidence that $\beta \ll a\gamma_{facet}$, and from this it appears likely that the ice/vapor ECS at temperatures $-40 < T < 0$ C will exhibit only small faceted regions. It also appears that $\gamma_{basal} \approx \gamma_{prism}$ (with an uncertainty of perhaps 20 percent, although it could be greater [10, 11, 12]), which means that the ECS is likely nearly spherical.

We note that several textbooks suggest that the ECS for ice/vapor is fully faceted [12, 11, 15]. This appears to be a misapplication of the Wulff construction, as the authors of these texts mainly considered the surface energy of the facets, even though the angular dependence of $\gamma(\hat{n})$ in its entirety is needed to calculate the ECS. In addition, the experiments cited in these texts as evidence for a faceted ECS were likely observing growth forms. The description of the ECS is similar in these three references, so it may have been propagated from one to the next over time.

We also note in passing that Landau has suggested that the equilibrium shapes of all crystals should be completely faceted at $T = 0$ [16, 17], a statement that is occasionally mentioned in the literature. However it appears that this theoretical result is unphysical for several reasons: 1) The time needed to reach equilibrium near $T = 0$ is so long as to be unrealizable in practice, and 2) the Landau model indicates that the surface energy $\gamma(\hat{n})$ has a cusp for all rational Miller indices, which would mean that $\gamma(\hat{n})$ is continuous everywhere but does not possess a well-defined derivative anywhere [17]. Thus the Landau theory seems to have little application to real experimental systems.

3 Equilibration Times

An important consideration for experimental studies of the ECS is the time required to reach equilibrium. For the case of ice, the equilibration process is somewhat similar to that occurring during the sintering of ice particles, since in both cases water molecules must be transported to reduce the overall surface energy of the system. Studies of ice sintering have shown that material transport via evaporation/deposition is substantially more rapid than via surface or bulk diffusion processes ([11], page 405), so we expect that evaporation/deposition will also be the dominant transport mechanism in reaching the ice ECS. (In contrast, for many metals that have been studied to date, surface diffusion is the dominant transport process in the relaxation to the ECS. This is because these metals are often chosen for their low vapor pressures, since this makes the experiments simpler. The vapor pressure of lead near its melting point, for example, is roughly 10^{10} times smaller than that of ice near its melting point.)

We can estimate the equilibration time via vapor transport by considering first the case of a slightly prolate spheroid, with major axis length $2(R + \varepsilon)$ and minor axis length $2(R - \varepsilon)$. We further assume an isotropic surface energy γ , so the ECS is a sphere. The equilibrium vapor pressure just above any point on the surface of this spheroid is

$$c_{eq} \approx c_{sat} \left(1 + \frac{2\delta}{R_{eff}} \right) \quad (1)$$

where c_{sat} is the saturated vapor pressure above a flat surface, $\delta = \gamma/c_{solid}kT \approx 1$ nm [13] and R_{eff} is the effective radius of curvature of the surface at that point. The vapor pressure difference between the “poles” and the “equator” of the spheroid is then approximately

$$\Delta c \approx \frac{2\delta\varepsilon}{R^2} c_{sat}$$

and it is this difference that drives the system to its ECS. The growth rate at the equator is then (using the notation in [13])

$$v_{equator} \approx \alpha v_{kin} \frac{2\delta\varepsilon}{R^2}$$

where α is the attachment coefficient at the growing surface. From this we see that the change in shape of the spheroid is given approximately by the differential equation

$$\frac{d\varepsilon}{dt} = -\alpha v_{kin} \frac{2\delta}{R^2} \varepsilon$$

which has the solution $\varepsilon(t) = \varepsilon_0 \exp(-t/\tau)$ with a time constant

$$\begin{aligned} \tau &= \frac{R^2}{2\alpha v_{kin} \delta} \\ &\approx 1.4 \left(\frac{R}{100 \mu\text{m}} \right)^2 \left(\frac{1}{\alpha} \right) \left(\frac{1 \text{ mm/sec}}{v_{kin}} \right) \text{ hours} \end{aligned} \quad (2)$$

Since $v_{kin} \approx 1$ mm/sec near the melting point [13], we see that the equilibration times will be of order hours for a 100 μm crystal with $\alpha = 1$, and perhaps a week for a 1 mm crystal. Unfortunately

we frequently have $\alpha \ll 1$, which then results in longer equilibration times. We consider several special cases:

Case 1: If the crystal is equilibrating in a background of air or some other inert gas, then α in Equation 2 should be replaced with

$$\alpha_{eff} = \frac{\alpha\alpha_{diff}}{\alpha + \alpha_{diff}}$$

where α_{eff} is an effective condensation coefficient that accounts for the diffusion of water molecules through the air, and α_{diff} is described in [13]. For a 100 μm crystal, $\alpha_{diff} \approx 0.001$ with a background pressure of one atmosphere. Clearly any ECS experiments with ice must be done in the absence or near absence of any background gas, or the equilibration times will be exceedingly long.

Case 2: If our initial crystal is a completely faceted prism, then reaching the ECS (assuming this is a nearly spherical shape) will require removing water molecules from the corners of the prism and depositing them on the facet surfaces. In this case there is a strong 2D nucleation barrier that retards deposition on the facet surfaces, whereas there is no nucleation barrier to removing molecules from the corners. Measurements of the growth of facet surfaces reveal that typically $\alpha_{facet} \approx \exp(-\sigma_0/\sigma)$, where σ is the supersaturation at the surface and σ_0 is determined experimentally [14]. Using $\sigma \approx 2\delta\varepsilon/R^2$ from the above discussion, we find prohibitively long equilibration times for crystals larger than even a few μm .

Case 3: If we start with a perfectly spherical crystal, then equilibrating to the ECS requires removing molecules from the facet surfaces (as they become exposed en route to the ECS) and depositing them on the rounded surfaces. In this case there is no nucleation barrier, and at low background pressures we would have $\alpha \approx 1$ in Equation 2.

Note that the nucleation barrier to reaching the ECS (Case 2) has also been studied in metal systems [18, 19, 1]. As with the ice case, it has been found that a nucleation barrier can effectively prevent a crystallite from reaching its ECS during the span of an experiment, and that the equilibration time is a strong function of the initial crystal morphology.

From these considerations we can identify a promising experimental path to observing the ECS for ice. This begins with a small columnar crystal prism, fully faceted, which can be easily grown. This crystal might be isolated by suspending it in an electrodynamic trap [20], or perhaps by placing the crystal on a suitable substrate in a sealed isothermal chamber. A superhydrophobic surface, for example, might be expected to cause only minimal perturbation of the equilibrium crystal shape.

The temperature of the experimental chamber would then be increased to near the melting point, where the prism facets undergo a roughening transition [21]. This would remove the nucleation barrier on the prism facets, and water molecules would thus be able to evaporate off the basal surfaces and deposit onto the prism facets or onto rounded regions, all with $\alpha \approx 1$. During this process one could optically monitor the transition to the ECS with time. Since the step energies are low near the ice melting point, the ECS at high temperatures would be nearly spherical. Once the ECS was obtained near the melting point, the temperature could then be lowered to observe the ECS at lower temperatures (Case 3).

In addition to normal crystallites, it is also possible to observe the ECS of “negative” crystals, or voids in a crystalline solid, as is commonly done in ECS studies. Here again we have several illustrative cases:

Case 4: If the initial ice void is a faceted prism, as is the typical shape when creating the void by evacuation [22], then the ECS must form by molecules being removed from the facet surfaces and deposited in the corners. In this case the initial removal of molecules is inhibited by a significant nucleation barrier, so the equilibration timescale is prohibitively long.

Case 5: If the initial ice void is spherical in shape, then molecules must be removed from the rounded surfaces and deposited on the growing facets, and both processes will proceed with no nucleation barrier.

Here again we see a promising route to achieving the ECS in a negative crystal. The process would begin with a columnar faceted void, which is a known growth form during evacuation [22]. A temperature gradient could be used to move the void away from its evacuation tube [29], thus isolating it inside the crystal in an evacuated state (i.e. with little or no background gas present). At this point the temperature would be raised above the prism roughening temperature, thus removing the nucleation barrier, and again the transition to the ECS could be monitored. Once a nearly spherical ECS was formed near the melting point, the temperature could then be lowered as described in the positive crystal case.

We note in passing that this ECS experiment requires a high degree of temperature uniformity. If an ice void of radius R is exposed to a temperature gradient ∇T , then one side of the void will grow while the other side evaporates, thus causing the void to move at a velocity

$$\begin{aligned} v &\approx \alpha v_{kin} \Delta\sigma \\ &\approx \alpha v_{kin} \frac{R}{c_{sat}} \frac{dc_{sat}}{dT} \nabla T. \end{aligned}$$

If we insist that a void moves by less than a distance R over the equilibration timescale, say 10 hours, then we must have $\nabla T < 0.005$ C/cm, which is a nontrivial temperature gradient to achieve in an experimental system.

We conclude that equilibration times of days or shorter could be achieved for both normal crystallites and crystal voids, provided suitable experimental conditions are applied. If a nucleation barrier inhibits the transition to the ECS, however, then the equilibration times are prohibitively long.

4 Experiments to Date

The ECS of ice has received little experimental attention thus far. Elbaum [21] reported observations of equilibrated ice crystals that were largely spherical, with facets forming a small fraction of the total surface area of the crystal. Out of equilibrium, the facets were found to be larger during growth, and smaller during sublimation, as one would expect. Few experimental details were given in this paper, unfortunately, so the reader is left guessing about equilibration times and observations of the transition from growth/melt forms to the ECS.

In contrast to the nearly spherical ECS observed by Elbaum, Colbeck reported a fully faceted ECS for ice [25], but a careful reading of this paper suggests several potential problems. For example, the crystals were fairly large and grown in air, so one expects exceedingly long equilibration times. Rounded plates were sometimes observed, and we would expect a substantial nucleation barrier for such crystals to achieve a full equilibrium shape. Also the experimental parameters were not especially well controlled, and the transition to the ECS as a function of time was not monitored. It is possible that these experiments were observing slow growth or evaporation forms, and not the true ice equilibrium shapes.

In another experiment Furukawa and Kohata [22] observed the formation of negative crystals, and these have been interpreted as showing a fully faceted ECS when the evacuation process was very slow or halted [23]. Again the paper does not elaborate on observations of the equilibration

times and the transition to the ECS, and again it appears possible that growth forms were being observed.

Kobayashi’s observations of ice crystal growth at low supersaturations [24] are frequently cited in the context of the ice ECS or the surface energy anisotropy, especially as a measurement of $\gamma_{\text{basal}}/\gamma_{\text{prism}}$ [12, 11, 15]. These measurements were made in air using a supersaturation of typically a few percent, however, which is substantially higher than the maximum supersaturation for observing the ice ECS (see below). Thus again these observations were likely of growth shapes, and not the true ice ECS.

In all these papers the lack of experimental details prevents one from understanding their contradictory results. Better experiments are clearly needed, and one would like to see careful observations of equilibration times and the transition to the ECS, especially as a function of temperature, crystal size, and initial conditions. Without this attention to detail, and publications that report these experimental details, we are not able to reach many definitive conclusions regarding the ice ECS.

The observations in [26] also suggest the occurrence of pyramidal facets on ice crystallites. However the images are somewhat unclear and the equilibration times used were very short. Measurements of atmospheric halos, and images of crystals collected during halo displays [27], show that the $\{10\bar{1}1\}$ pyramidal facets do occur during ice crystal growth at low temperatures, suggesting that these facets may also appear in the ECS. However these observations were likely all of growth forms, so they may in fact have no bearing on the ECS.

Numerous observations have been made of bubbles in ice, sometimes in the laboratory and sometimes in very old ice formations [28, 29, 30]. To my knowledge, however, neither spherical nor partially faceted shapes have been seen in these samples, so it appears that these bubbles also did not possess true equilibrium shapes.

My conclusion is that none of the observations or experiments to date has conclusively demonstrated the ECS for ice. This is not surprising, since our discussion above suggests that the equilibration times should be quite long except in special circumstances. Plus there simply has not been much experimental effort aimed at the ice ECS, in contrast to simple metal systems. But although the ice ECS has not been definitively observed to date, it does appear that successful experiments are possible if sufficient care is taken.

5 Ice Growth Dynamics

Our final question, somewhat tangentially related to the ice ECS, is regarding what role the anisotropic surface energy plays in ice crystal growth from water vapor. We expect that if the growth rate is low enough, or if the crystal size is small enough, then surface energy effects will begin to overshadow kinetics effects in determining growth rates and morphologies. Our question is then one of determining what physical mechanisms control the ice growth behavior in what regions of parameter space.

Let us first consider the slow growth of a faceted ice crystal, a simple hexagonal prism. We will assume the absence of any inert background gas, so water vapor diffusion does not limit the growth. Since the equilibrium vapor pressure of any point on the ice surface is given by Equation 1, we see that c_{eq} will be highest at the corners of the prism. This is a surface energy effect, and if the applied supersaturation σ is less than $\sigma_{\text{corner}} = (c_{eq,\text{corner}} - c_{\text{sat}})/c_{\text{sat}}$, then the corners will become more rounded with time. However if $\sigma > \sigma_{\text{corner}}$, then crystal growth will cause the corners to become less rounded. Thus from Equation 1 we see that the corner radius for a growing crystal prism will

be approximately

$$R_{corner} \approx \frac{2\delta}{\sigma}.$$

If R_{corner} is greater than the overall size of the crystal, then the crystal morphology will be essentially the ECS. At smaller values of R_{corner} , the morphology will be essentially an ice prism with slightly rounded corners. Taking $R_{corner} = 2 \mu\text{m}$ in this expression gives $\sigma = 0.1$ percent. Put another way, we expect that surface energy effects will dominate only at supersaturations below a maximum of $\sigma_{\max} \approx 2\delta/R_{eff}$, where R_{eff} is the characteristic size of a growing crystal feature. Typically $\sigma \gg \sigma_{\max}$ in ice growth experiments, so we would expect surface energy effects are much smaller than kinetic effects in determining the growth dynamics and crystal morphologies.

If we add that the growth velocity is given by $v \approx \alpha v_{kin} \sigma$ [13], the above expression tells us that surface energy effects will begin to dominate if

$$\begin{aligned} v R_{eff} &< 2\alpha\delta v_{kin} \\ \left(\frac{v}{1 \mu\text{m/sec}}\right) \left(\frac{R_{eff}}{1 \mu\text{m}}\right) &< \alpha \end{aligned}$$

where R_{eff} is the size of a growth feature, and in the last expression we took $v_{kin} = 500 \mu\text{m/sec}$. Again, this inequality is not satisfied in essentially all ice growth experiments done to date.

Another way of addressing this question is to consider the growth of a dendrite tip, which has a growth velocity (see Equations 24-28 in [13])

$$\begin{aligned} v &\approx \frac{2D}{RB} \frac{c_{sat}}{c_{solid}} \left[\sigma_{\infty} - \frac{2\delta}{R} - \frac{v}{\alpha v_{kin}} \right] \\ &\approx \frac{2D}{RB} \frac{c_{sat}}{c_{solid}} \left[\sigma_{\infty} - \frac{2\delta}{R} - \frac{\sigma_{\infty} R_{kin}}{\alpha R} \right] \end{aligned} \quad (3)$$

where

$$R_{kin} = \frac{2D}{B} \sqrt{\frac{2\pi m}{kT}} \approx 30 \text{ nm}$$

For typical atmospheric growth we have $\sigma_{\infty}/\alpha (\sigma_{surf}) > 1$, so the kinetics term in Equation 3 is roughly an order of magnitude larger than the surface energy term. Using direct measurements of dendritic growth (see the discussion following Equation 31 in [13]) again shows that the kinetics term is roughly an order of magnitude larger than the surface energy term.

Our overall conclusion from this analysis is that attachment kinetics are more important than surface energy in determining ice crystal growth rates from water vapor, by roughly an order of magnitude for typical experimental or atmospheric conditions. Furthermore, to my knowledge no experiments to date investigating ice crystal growth from water vapor have conclusively observed any surface energy effects. In part this is because vapor diffusion and surface attachment kinetics are dominant effects, but also evaporation (with $\sigma < 0$) can produce rounded shapes that are essentially indistinguishable from surface energy rounding (which occurs during growth, when σ is small but still positive). As with the ECS, measurements of surface energy effects in ice growth dynamics from the vapor phase are likely observable in conditions of very slow growth of very small crystals, but so far have not been definitively observed.

6 Conclusions

Based on the above analysis, we reach the following conclusions regarding the ice ECS, the anisotropic surface energy, and surface energy effects on ice crystal growth from water vapor.

The ECS has not yet been definitively observed for ice crystals. This conclusion stems from the many observations of the ECS in metal systems, our theoretical understanding of those systems and its application to the case of ice in water vapor, and the fact that the experiments to date have not made a convincing case for the observation of the ice ECS. An examination of ECS measurements in metals suggests that the experiments are quite difficult, and it is easy to mistake growth/evaporation forms for the ECS. Experiments to date in ice have not monitored the transition to the ECS as a function of time, and have probably underestimated the time needed to reach the ECS.

The surface energy anisotropy is likely cusp-like near the faceted surfaces, and the size of the cusps can be estimated from crystal growth measurements. Again this conclusion stems in part from our theoretical understanding of the ECS in other systems, which in turn comes from ECS experiments. Comparing with metal systems and the step energy measurements described above, the evidence suggests that $(\gamma_{\max} - \gamma_{\min})/\gamma_{ave}$ in ice is no larger than 5-10 percent. The standard model for the ECS (developed largely from metal systems) includes cusps in $\gamma(\hat{n})$ at the facet angles. It is highly likely that this model applies to ice as well, so that the sizes of the facet cusps can be estimated from step energy measurements.

The equilibrium shape is likely nearly spherical with only small faceted regions. Measurements of ice step energies allow an estimate of the cusps in $\gamma(\hat{n})$, and the sizes of the faceted regions follow from the Wulff construction, as described above. The result is that only a small fraction of the ice ECS is faceted, with the fraction becoming larger at lower temperatures.

Given the poor state of ice ECS experiments, it remains possible (I believe somewhat remotely) that γ_{basal} and γ_{prism} are both substantially lower than $\gamma(\hat{n})$ at angles far from the facet angles, and in this case the ECS would indeed be fully faceted, or nearly so. However the preponderance of the evidence suggests that the surface energy anisotropy is small. The fact that ice does not readily cleave along facet surfaces further supports this conclusion. Accurate observations of the ECS could remove the remaining uncertainties.

The time needed to reach equilibrium is likely prohibitively long, except under special circumstances. As described above, there are substantial 2D nucleation barriers that prevent the growth of facet surfaces at low supersaturations. These nucleation barriers have been observed in ice growth measurements, which reveal their size and temperature dependence. (Note that this assumes the absence of any dislocations, which was one of our initial assumptions in this examination of the ice ECS. This assumption is warranted from an experimental standpoint because growth measurements have shown that dislocations are relatively rare in small ice crystals [14].) The same nucleation barriers are present in metal ECS systems, and they have been shown to have substantial effects on the equilibrium times in these systems. However, the roughening transition on the prism facets for $T > -2$ C gives a possible route to achieving the ECS in ice, as described above.

Surface energy effects likely play a relatively smaller role in ice crystal growth dynamics when compared to the role of attachment kinetics. This conclusion follows from an examination of ice crystal growth experiments and ice growth under atmospheric conditions, as described above. Effects from attachment kinetics are roughly an order of magnitude larger than effects from surface energy under typical conditions. Surface energy effects are expected to domi-

nate only for extremely small crystals (of order microns in size or smaller) and when the growth is extremely slow (so that the growth morphology is only slightly changed from the ECS). In addition, the surface energy anisotropy is likely small, of order a few percent, while the anisotropy in the attachment kinetics is typically far greater. Since many morphological features arise from anisotropies, this further supports the statement that attachment kinetics is substantially more important than surface energy effects in governing ice growth.

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